

EP 0 156 924 B1



Europäisches Patentamt
European Patent Office
Office européen des brevets



⑪ Publication number:

0 156 924 B1

⑫

EUROPEAN PATENT SPECIFICATION
published in accordance with Art.
158(3) EPC

⑯ Date of publication of patent specification: 17.04.91 ⑮ Int. Cl. 5: C09K 3/00, A23L 3/34,
A01N 59/16, A61L 9/01,
B01J 20/02, B01J 20/22,
B27K 3/52, C08J 5/18,
C09K 21/10, D21H 21/34,
D21H 21/36

⑯ Application number: 84903563.9

⑯ Date of filing: 25.09.84

⑯ International application number:
PCT/JP84/00457

⑯ International publication number:
WO 85/01512 (11.04.85 85/09)

⑭

CHEMICALLY ACTIVE COMPOSITION CONTAINING FERROUS ION.

⑯ Priority: 24.09.83 JP 176624/83
24.03.84 JP 56490/84
27.03.84 JP 57408/84
17.07.84 JP 148363/84
01.09.84 JP 183511/84
20.09.84 JP 197043/84

⑯ Date of publication of application:
09.10.85 Bulletin 85/41

⑯ Publication of the grant of the patent:
17.04.91 Bulletin 91/16

⑯ Designated Contracting States:
AT BE CH DE FR GB LI LU NL SE

⑯ References cited:
JP-A- 5 959 604
JP-A-54 122 687

⑯ Proprietor: THE STATE OF JAPAN, as Represented by the DIRECTOR GENERAL of the AGENCY of INDUSTRIAL SCIENCE and TECHNOLOGY
3-1, Kasumigaseki 1-chome Chiyoda-ku Tokyo 100(JP)

Proprietor: MINATO SANGYO CO. LTD.
7-1, Kasumigaseki 3-chome Chiyoda-ku, Tokyo 100(JP)

⑯ Inventor: IKARI, Yoshikatsu, c/o Agency of Ind.Sc.&Techn.
Nat.Chem.Lab.for Ind., Higashi 1-chome Yatabe-machi, Tsukuba-gun, Ibaraki-ken(JP)
Inventor: YOKOYAMA, Shoichiro, c/o Agency of Ind.Sc.&Techn.
Nat.Chem.Lab.for Ind., Higashi 1-chome Yatabe-machi, Tsukuba-gun, Ibaraki-ken(JP)

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

JP-A-54 132 246
JP-A-55 111 408
JP-A-59 132 937

WO 82/03817

Inventor: OHAMA, Chiaki, c/o Minato Sangyo
Co.Ltd.

7-1, Kasumigaseki 3-chome
Chiyoda-ku, Tokyo 100(JP)

Inventor: FUKUI, Ryosuke, c/o Minato Sangyo
Co.Ltd.

7-1, Kasumigaseki 3-chome
Chiyoda-ku, Tokyo 100(JP)

⑦ Representative: Boeters, Hans Dietrich, Dr. et
al
Boeters & Bauer Bereiteranger 15
W-8000 München 90(DE)

Description

This invention relates to a novel composition containing divalent iron ions having various chemical and physiological effects such as deodorization, bactericidal action, freshness-preservation of foods, promotion of plant growth and flame-proofing (flame-retardation) of flammable materials.

Background Art

Iron (II) compounds such as ferrous sulfate have a wide variety of utility. However as is well-known, divalent iron ions have the characteristic, when in the form of aqueous solution, of readily undergoing oxidation by dissolved oxygen or air to turn yellowish brown and result in precipitation. It has been practiced to incorporate hydroxylamines, tin compounds or the like as reducing agents in order to avoid the oxidation of the ferrous ions in the aqueous solution but, since these substances are highly toxic to the human body, applications for aqueous solutions containing divalent iron ions have been limited.

The present inventors have proposed a chemically active aqueous solution and a solid substance containing a small amount of L-ascorbic acid together with divalent iron ions as a composition in which an aqueous solution containing divalent iron ions is stabilized and provided with various functions (PCT/JP83/099: Japanese Patent Laid-Open No. 132937/1984). However, since this composition itself is an aqueous solution, the storage and the handling of the solution has been troublesome and the method of use has been restricted to impregnation and dipping using water absorbing material as the carrier in the case of the solid matter.

Disclosure of Invention

The first object of this invention is to provide a composition of an aqueous solution containing divalent iron ions and the dried product thereof (powder, granules) which is further stabilized while maintaining activities. The second object of this invention is to provide new application uses for the thus stabilized chemically active composition containing divalent iron ions. The third object of this invention is to provide novel multi-function materials equipped with one or more functions at the same time by applying the chemically stable and stabilized composition.

Accordingly this invention relates to a chemically active composition containing divalent iron ions capable of satisfying the foregoing objects, being extremely stable and having various chemical and physiological activities such as deodorization, bacteriocidal action, preservation of freshness of foods, growth promotion of plants and flame-proofing treatment (flame-retardation) for flammable materials. Specifically it relates to a composition containing divalent iron ions, wherein a water-soluble iron (II) compound, alum and ascorbic acid and/or citric acid are contained, and the ratio between the divalent iron ions in the iron (II) compound and ascorbic acid or citric acid is between 1:0.02 and 0.30 (in the case of ascorbic acid) or 1:0.01 and 0.80 (in the case of citric acid) by weight ratio; and wherein the alum is contained within a range up to 100 % by weight based on the total amount of the iron (II) compound, ascorbic acid and/or citric acid.

Examples of the iron (II) compounds which can be used in the composition according to this invention, are iron (II) salts of inorganic acids such as ferrous sulfate, ferrous chloride, ferrous nitrate, ferrous bromide and a ferrous iodide, as well as iron (II) salts of organic acids such as ferrous gallate, ferrous malate and ferrous fumarate. However, the iron (II) compound are not restricted only to those exemplified above, but any of the compounds may be used so long as they can be dissolved in water to form divalent iron ions.

While L-ascorbic acid and D-isoascorbic acid are used as ascorbic acid, L-ascorbic acid is preferred.

In this invention, ascorbic acid and citric acid may be used singly or in combination. In the case of the combined use, citric acid may be used in a small amount since it acts in an auxiliary manner as a stabilizer to ascorbic acid.

In this composition, the weight ratio of the iron (II) in the iron (II) compound and ascorbic acid is preferably between 1 : 0.02 and 0.13 (about 0.006 - 0.04 mol of ascorbic acid per one mol of ferrous salt by molar ratio) and, more preferably, between 0.05 and 0.13 (0.016 - 0.04 mol of ascorbic acid per one mol of ferrous salt by molar ratio). If ascorbic acid is used in excess of the upper limit in this invention, the composition is pigmented, which reduces its economical value and the freshness-preserving and deodorizing effects, and the stability are also reduced. While on the other hand, if it is less than the lower limit, the stability of iron (II) is insufficient. Further, in the case of citric acid, the weight ratio of iron (II) in the iron (II)

compound is preferably in a range between 1 : less than 0.80 and, more preferably, in a range between 1 : 0.01 and 0.8. As an example, the relationship between the molar ratio of L-ascorbic acid (H₂ Asc) to the iron (II) compound in the composition according to this invention to the deodorizing effect (NH₃ adsorption amount) is shown in Figure 1).

5 In order to develop the activities of the composition according to this invention, it is required that the iron (II) compound, ascorbic acid or citric acid and alum are combined. This can be attained by dissolving each of the ingredients in a predetermined ratio in water to prepare an aqueous solution. Alternatively, the aqueous solution may be converted into powder through usual spray drying, freeze drying.

10 The alum in the iron (II) compound composition according to this invention has a flame retarding effect, and stabilizes the deodorizing effect as well. The amount of alum to be added may vary depending on the application uses and the forms of the composition according to this invention, but the range between 2 and 100 and especially 2 and 20 % by weight being preferred. While there is no particular restriction for the alum, potassium alum, ammonium alum, sodium alum or the like are preferred, the burnt alum being particularly preferred.

15 Further, the deodorizing effect and the flame proofing effect of the composition according to this invention can further be improved by preferably incorporating a predetermined amount of sodium chloride. The amount to be added preferably ranges from 0.5 to 15 % by weight based on the total amount of the iron (II) compound and ascorbic acid or citric acid.

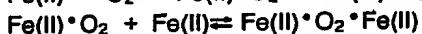
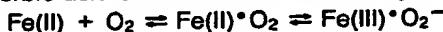
20 The composition according to this invention is provided as an aqueous solution or the dried product thereof (powder, granules, etc.).

25 The concentration of the divalent iron ions in the aqueous solution, in view of the unique chemical activities of the aqueous solution, is generally more than 0.15 % by weight and, preferably, more than 0.3 % by weight calculated as metal iron and the upper limit thereof is defined by the solubility of the (II) compound.

30 Since the composition according to this invention comprises a system of iron (II) compound - ascorbic acid and/or citric acid - alum, the divalent iron ions are extremely stabilized while remaining in an activated state. Accordingly, no substantial precipitation is formed even when the aqueous solution is brought into contact with air for a long period of time. Further, since the divalent iron ions are stabilized, they can endure processing treatment at a high temperature such as spray drying, also the dried powder or the like, this obtained is stable under oxidative conditions, and shows substantially the same extent of deodorizing and other similar activities as the aqueous solution. Further, the dried substance requires no carrier or the like and it is a highly concentrated agent comprising 100 % effective ingredients. Accordingly, it can be used not only by being dissolved again into water, but also by being kneaded and mixed directly with cosmetics, pharmaceuticals, flame-retardants or resins.

35 Accordingly, upon using the composition according to this invention, any of the methods can be selected such as impregnation on a support, coating, dipping, spraying, kneading and the like and it can be used broadly for such application uses as deodorization, flame retardation, freshness preservation and growth promotion.

40 Although the reason why the composition according to this invention exhibits the unique activities as described above is not yet clear at present, it is supposed that the molecular oxygen is converted into a super-oxide (O₂⁻) with a strong oxidative power under the action of the divalent iron ions in the presence of ascorbic acid or citric acid as shown by the following schemes and this is kept in a stable state:



45 Further, it is considered that the bactericidal effect due to the super oxide also makes a contribution. While the mechanism of the flame-retarding effect is not clear at present, it is estimated that sodium chloride has a specific effect.

50 The composition according to this invention will now be described more specifically for the respective effects. (Deodorant)

55 The deodorant comprising the aqueous solution or the dried product thereof of the composition according to this invention can be applied for the purpose of eliminating offensive odors in toilets, garbage pails, refrigerators, drainage openings or the likes, as well as for the removal of offensive odors inside a room. As regards the method of application of the deodorant, the aqueous solution may be used to spray out or wash the source of offensive odor. In the case of a solid form, it may be applied directly to the source of offensive odor or, in addition, it may be placed in a space containing offensive odor. The above mentioned deodorant may also be used by incorporating it in part of a sanitary material such as a diaper or sanitary napkin.

As compared with the ordinary aqueous solution containing divalent iron ions, the aqueous solution of the composition according to this invention exhibits various unique chemical and physiological activities, which include significantly high deodorizing effect against offensive odor substances containing sulfur or nitrogen, for example, hydrogen sulfide, methylmercaptan, ammonia and trimethylamine. In order to form a solid deodorant, paper, synthetic paper, cloth, non-woven fabric, porous filler or similar other solid material may be impregnated with the aqueous solution, followed by drying treatment. In this case, the drying treatment may be omitted depending on the cases. The porous fillers can include activated carbon, zeolite, bentonite, kaoline, perlite, sepiolite, diatomaceous earth, silica, alumina and the like and they can take any desired form such as powder or granules. The total amount of L-ascorbic acid or citric acid, the iron (II) compound and alum carried on the solid substance is from about 0.5 to about 20 parts by weight as the solid component based on 100 parts by weight of the solid substance.

(Flame-retarding agent)

This can be prepared by impregnating into flammable materials such as papers, fabrics (carpet, curtain, etc), fibers, yarns, woods, urethane resins and the like with the aqueous solution of the composition according to this invention by means of treatment such as coating, spraying and dipping. Further, the composition according to this invention may be kneaded as the dried product with a resin and formed, for example, into a film, or it may be spun after being mixed in a synthetic resin. The content of the retarding agent in the material to be treated, while differing depending on the purpose of treatment, the application use of the material to be treated and the kind of the material, preferably ranges usually from 5 to 70 parts by weight based on 100 parts by weight of the material to be treated.

In this case, the material to be treated is given a flame retarding effect and a deodorizing effect together to produce a multi-functional material.

(Freshness-preserving agent)

The third unique effect of the composition according to this invention is the freshness-preserving effect and bactericidal activity. When the aqueous solution according to this invention is applied to fresh foods such as vegetables, fruits, meats, shellfish, or their processed foods, these foods can be maintained at high degree of freshness over a prolonged period of time. In this case, the aqueous solution may be applied by coating or spraying it on to the foods or by dipping foods in the aqueous solution. Similarly to the above-described case of the solid deodorant, a solid material such as papers, synthetic papers, woven fabrics, non-woven fabrics, yarns and porous fillers may be impregnated with the aqueous solution and then subjected to drying treatment in order to form a solid freshness-preserving agent. Regarding the application method of such a solid freshness-preserving agent, in the case of the sheet- or film-like form, for example, a sheet or film may be used to wrap the foods. While on the other hand, in the case of the powdery or granular form, it may be admixed with appropriate chemicals. Furthermore, the foods may be wrapped with a film of resin kneaded with the dried product of the composition according to this invention.

Furthermore, the freshness of the foods can also be preserved by placing them within a steam atmosphere of the aqueous solution of the composition according to this invention. In this case, the total concentration for the iron (II) compound, ascorbic acid or citric acid and alum as the effective ingredients in the aqueous composition, while different depending on the kind of the foods, intensity of treatment, transferring velocity of the atmosphere and the like, lies within a range usually between from 0.1 to 40 % by weight and, preferably, from 1.0 to 20 % by weight. Further, the humidity in this case is usually more than 80 % and, preferably, more than 90 %. Further, although there is no particular restriction for the temperature, excessively high temperature is undesirable and a temperature lower than the ambient temperature is preferred.

In addition, the steam atmosphere is preferably circulated forcibly as required, and it is particularly preferred to replace a portion of the steam atmosphere always with fresh atmosphere so that the atmosphere containing the above-described effective ingredients is kept active. This can be attained specifically by releasing a portion of the atmosphere through at least one gap formed in a vinyl plastic housing. However, the atmosphere is basically kept closed tightly.

The freshness-preserving agent is suitable to the application of freshness-preservation, antiseptic treatment and preservation for perishable foods such as vegetables, fruits, meats and shellfish or kneaded marine products. Specifically, this method can also be applied to the display case in a Sushi shop and the

show case in a meat source or butchering. Since this method uses no harmful bacteriocides at all and comprises a combination of ingredients safe to men and animals, it can be used not only during transport from producing districts to markets but also by end users such as house wives with no risk. Accordingly, it is particularly advantageous for setting up a consistent freshness-preserving system from the producing districts to the consumers. Further, the use of the freshness-preserving agent is advantageous in that it does no harm to the human body at all ensuring safety even if the steam atmosphere leaks out of the system.

10 (Growth promoting agent for plants)

The unique physiological activity of the composition according to this invention resides in the effect of promoting the plant growth. In this case, while there is no particular restriction in applying the composition according to this invention, there are methods, for instance, of placing plants in the steam atmosphere, as well as a method of watering the plants with the aqueous solution of the composition.

In using the composition of the plant growth promoting agent as an aqueous solution, the total concentration of the iron (II) compound, ascorbic acid or citric acid and alum as the effective ingredients in the solution, while different depending on the kind of the plants to be treated, amount of treatment and the transferring velocity of the atmosphere, usually ranges from 0.1 to 40 % by weight, preferably, from 1.0 to 20 % by weight.

For carrying out the growth promotion and the activating treatment for plants by the composition according to this invention, a steam atmosphere at high humidity is formed with the aqueous solution of the composition, for example, in which flowers and ornamental plants are placed. In this case, the humidity is usually more than 70 % and, preferably, more than 90 %. Further, although there is no particular restriction, excessively high or low temperature is undesirable and it ranges usually from 10 to 20 °C and, preferably, from 16 to 18 °C.

In this case, although it is preferred to appropriately circulate the steam atmosphere forcibly it is particularly desired to always replace a portion of the steam atmosphere with fresh atmosphere so that the atmosphere containing the effective ingredients is maintained in an active state. This may be attained by forming the atmosphere within a vinyl plastic housing or the like and forming gaps at least at a portion thereof. However, the atmosphere is basically kept closed tightly.

Although it is preferred that the treatment is carried out by forming the steam atmosphere within a transparent vinyl plastic film or the like as described above and permeable to sunlight, the purpose can sufficiently be achieved even within a room.

The above-described method has a feature capable of promoting the growth of stalks and buds of the flowers and ornamental plants in a quick acting manner. Further, the method according to this invention has an effect as an important merit thereof of improving the quality of the flowers and ornamental plants, since it can activate the potted plants to recover the intense green color and the luster of leaves, which have once become less vigorous being placed in the room or the like. Further, it is preferred to water paddy field rice plants or the likes with the diluted aqueous solution according to this invention.

Functional materials obtained from the composition according to this invention will be explained next taking plastic films and wallpapers as examples.

45 (Preparation of plastic film)

A plastic film is prepared by incorporating a composition comprising the iron (II) compound, ascorbic acid and/or citric acid and alum into a resin.

The resin usable herein may either be a synthetic resin or natural resin. Specific examples can include polyolefins such as polyethylene and polypropylene, polyvinyl compounds such as polyvinyl alcohol, polyvinyl chloride, polyvinylidene chloride, polystyrene, and vinyl chloride - vinyl acetate copolymers, cellulose esters such as cellulose diacetate, regenerated cellulose, polyesters, polyamides, hydrochloride rubber, natural rubber and fluorine resins.

While varying depending on the application use and the material of the film, a preferred film thickness usually ranges from 0.01 to 0.5 mm but films outside the above-mentioned range can also be prepared.

In the description of the present specification and claims, the term "film" does not mean to particularly restrict the thickness but it includes any so-called sheet-like material. Further, the term "plastic" does not mean thermoplasticity but means high molecular materials in the broader sense.

The content of the composition according to this invention in this film is preferably more than 0.5 % by weight calculated as the solid component. A higher upper limit is better but the film becomes cloudy in excess of 5 % by weight, although with no particular problems for the freshness-preserving and deodorizing effects.

5 The plastic film can be prepared, in addition to the admixture of the composition according to this invention as a dried product, by ordinary film-forming processes, for example, calendering method, T-die method, inflation method and solution casting method. In the case of the inflation method for instance, the iron (II) compound composition is preferably incorporated first at a high concentration in the master pellet, which is further incorporated with a resin to dilute the concentration to about 1/10, followed by melt 10 extrusion molding.

10 Further, it is also possible to add customary ingredients such as plasticizer, stabilizer, filler and other additives (such as pigment), within such a range as far as they do not impair the development of the activities of the composition according to this invention. If it is required to accelerate the development of the 15 activities of the composition according to this invention, from 3 to 10 % by weight of sodium chloride may be added by mixing.

15 The thus obtained plastic film is a transparent film substantially identical in appearance to that containing no iron (II) compound composition, although the smoothness is somewhat reduced. The use of the plastic film can provide an excellent effect capable of preserving the freshness of foods for a long period of time to prevent perishing thereof. The film may preferably be applied for preserving the freshness, 20 prevention of perishing and preservation of perishable fresh foods such as vegetables, fruits, meats and shellfish or kneaded marine products by packing and containing them therein. More specifically, it can be used as the casing film for fish pastes (Kamaboko), sausages or the likes. The material obtained according to this invention uses no harmful bacteriocides at all and comprises a combination of ingredients safe to men and beasts. Further, the film also has a deodorizing effect to adsorb and remove the offensive and 25 peculiar odors of foods.

(Preparation of functional wall paper)

30 A functional wall paper can be prepared by applying a coating of or incorporating the composition according to this invention in wall paper material.

35 There is no particular restriction for the wall paper material usable in this invention and those conventionally employed so far can be used. While flame-retardant vinyl chloride resins are most preferred for the surface decorative layers, but urethane resin, acrylic resin, polyethylene resin, polypropylene resin and polyester resin may also be used non-limitatively. Further, any of flame retardant papers, synthetic papers, inorganic papers and woven fabrics may be used as the substrate base cloth. In summary, any of wall paper materials to which the iron (II) composition can be applied may be used.

40 Typical examples for the blend of the wall paper material made of vinyl chloride resin, which are most preferred among them, are shown.

45

50

55

	Blend (A)	Parts by weight
5	Vinyl chloride resin	100
10	Plasticizer (containing flame retardant plasticizer)	60
15	Foaming agent (ADCA)	5
20	Stabilizer	3.5
25	Filler	10
30	Flame retardant	3
35	Pigment	30
40	<hr/> Total	211.5

	Blend (B)	Parts by weight
25	Vinyl chloride resin	100
30	Plasticizer (containing flame retardant plasticizer)	55
35	Foaming agent (OBSh)	2
40	Stabilizer	2
45	Filler	50
50	Flame retardant	3
55	Pigment	20
60	<hr/> Total	232

Then, the iron (II) composition is applied by coating of or incorporating it in the wall paper.

The coating may be applied by any method and preferred method include two types, that is, a method of utilizing a gravure printer and a method of applying coating by a doctor knife. The complete step sequence for each of them is shown below.

(a) Method of utilizing a gravure printer

Coating → gravure printing → embossing
 (vinyl chloride
 5 sol coat)

10 printing (patterning) → embossing
 printing (white ink) → embossing
 coating (sol coat) → embossing →
 → punctuation (using needle roll)

After gravure printing, it is dried at 120 - 130 °C for 30 - 60 sec.

(b) Spanishing method by using a doctor knife

coating → embossing → spanishing
 20 printing → embossing → spanishing

After spanishing, it is dried at 130 - 140 °C for 1 - 1.5 min.

Upon such coating, an aqueous ink containing the composition according to this invention is used.

26 In the case of using the composition according to this invention as an aqueous solution, the concentration of the solid content is up to 30 % by weight at the maximum in view of the relationship with the solubility. Since the aqueous ink may possibly become gelified if the solid content is too high, the amount is less than 30 % by weight and, preferably, 25 % by weight and, in view of the fabrication stability, preferably from 15 to 20 % by weight. As the basic composition for the aqueous ink, those blendings of the gravure aqueous ink known so far can be employed.

30 An example of the aqueous ink blended with the composition according to this invention is shown below.

Ingredient	Parts by weight
VPA G medium	90
" " color	10
40 Aqueous solution of the composition according to this invention (solid content 20 %)	20
Total	120

45 (note) VPA G medium : resin component (vinyl chloride -
acrylic copolymer) 22 %

50 VPA G color : resin component (ditto) 18 - 24 %
pigment content 3 - 15 %

55 The coating amount of the aqueous ink in the gravure printing method (a) as described above, ranges usually from 10 to 40 g·m² and, preferably, from 20 to 30 g·m². Further, in the above-described spanishing method (b) using the doctor knife, it ranges from 20 to 70 g·m² and, preferably, from 30 to 50 g·m². In this case, if the coating amount is in excess of 70 g·m², it causes a problem to the ink adhesion and

the stability of the chromaticity at the surface and, while on the other hand, if it is insufficient the intended result cannot be obtained.

5 Next, the composition according to this invention may be used as powder. In this case, for instance, it may be blended, for example, in the paste sol of a vinyl chloride resin, into a paint composition, which is then applied to the wall paper material with or without dilution to an appropriate concentration. One example of such painting composition is shown below.

	Ingredient	Parts by weight
10	Vinyl chloride paste resin	100
	Plasticizer	50
15	Stabilizer	2
	Composition according to this invention	20
20	(ferrous fulfate : L-ascorbic acid = 1 : 0.03 (molar ratio), alum 10 % by weight, particle size of several tens of micrometer)	
	Pigment	20
25	Total	192

30 While it is required to apply a strong shearing force for dispersing the paint composition (for instance, by passing through paint rolls), the paint thus prepared can be used in the same manner as usual vinyl chloride paste sols.

The steps other than the coating step by the gravure printing or spanishing method, for instance, the steps of printing and embossing can be performed in the same manner as in the conventional preparation of wall papers.

35 Depending on the kinds of the wall paper material, the powder of the iron (II) composition may directly be kneaded into the wall paper material.

In this way, interior material provided with unique functions (air cleaning, deodorization, sterilization, mold prevention) can be obtained.

40 The advantages of the wall paper thus obtained reside not only in improving the aesthetic appearance of a room but also in cleaning the surrounding atmosphere and generating active oxygen which is strongly preferred biochemically. Although the deodorizing effect is one of the factors in this invention, this does not represent the entire effect but is a measure for each of the effects based on the active oxygen. Further, by applying punctuation to the wall paper, air cleaning effect such as deodorization can be maintained for a long period of time.

45 Further, the wall paper has a flame proofing effect. Moreover, it maintains the activity capable of enduring heating such as emboss fabrication and foaming fabrication.

While the wall paper can be used in the same manner as ordinary wall paper, it is particularly useful preferably for the living rooms and toilet in ordinary houses, sick rooms and wards in hospitals.

50 **Brief Description of the Drawings**

Figure 1 is a graph showing the relationship between the molar ratio of L-ascorbic acid (H_2 Asc) to iron (II) compound in the composition according to this invention and the deodorizing effect (NH_3 adsorption amount), and Figure 2 is an explanatory view of an apparatus for a deodorizing test.

55

Best Mode for Carrying Out the Invention

This invention will next be described more specifically referring to examples.

Example 1

5

(i) Preparation of Aqueous Solution

(a) Solution A

10 After dissolving 27.5 g of ferrous sulfate heptahydrate (molecular weight 278.03) in water to 100 ml, 0.5 g of L-ascorbic acid were added and dissolved to prepare an undiluted solution, which was diluted to twice the volume with water.

(b) Solution B (composition according to this invention)

15 After adding 10 g of burnt alum to 100 ml of the undiluted solution (a) above and stirring for 30 min, they were centrifugally separated and filtered. The thus obtained filtrate was diluted to 2.5 times the volume with water.

(c) Solution C

After adding 10 g of burnt alum to 100 ml of water and mixing for 30 min, they were centrifugally separated and filtered. The thus obtained filtrate was used.

20 (d) Solution D

27.5 g of ferrous sulfate were completely dissolved in 100 ml of water, which was diluted to twice the volume with water.

26 (ii) Preparation of Treated Paper

The solutions A - D prepared as above were given separately into watch glass plates each with 9.3 cm diameter, in which Toyo Filter Papers Teisei No. 2 (9 cm diameter) were immersed for 30 min and then spontaneously dried over one night. In this way, treated papers A - D with the deposition amount about from 30 27 to 28 to 100 of the filter paper weight before treatment were obtained as shown in Table 1. Of the thus obtained treated papers, paper D turned yellow, while papers A, B turned pale brown and paper C remained white.

35 (iii) Flame-proofing Test

A flame of a flame height of 4 cm was produced by using a gas burner with 1 cm inner diameter and not mixing air with the gas and the treated papers A - D each cut into a size of 1 cm width and 5 cm length were put into the flame from the top end of the flame for 2 cm length and the state when taken out from the flame was observed. The results are shown in Table-1.

45

50

55

Table 1

Treated paper	Amount deposited	The state of the residual flame and the degree of combustion after taking out from the flame
A	27.5	Burnt with flame. Continued to burn gradually after the flame was extinguished and completely consumed in about 25 sec, to leave reddish brown ash.
B	28.5	No flame. Gradually burnt and consumed in about 60 sec, to leave reddish brown ash.
C	26.6	Burnt with flame. Burnt for 7 sec after the flame was extinguished, it carbonized.
D	26.3	Burnt while entirely surrounded with the flame. Continued to burn for 20 sec after the flame was extinguished, to leave a reddish brown ash.

(note) The deposition amount is represented by % relative to the weight of the paper before treatment.

35

(iv) Deodorizing Test

40 Filter paper of 20 cm x 29.5 cm (10 g weight) was treated by using 2.5 times dilution solution of the solution B (without the last 2.5 times dilution in the above-mentioned preparing method) to prepare treated papers in the same manner as described above. The deposition amount relative to the weight of the paper before treatment was about 50 % by weight. The paper was cut into various sizes and placed in a vinyl plastic bag and tested for the deodorizing effect while adding 1 ml of aqueous ammonia (28 % concentration). The results are shown in Table 2.

50

55

Table 2

Size of the treated paper (cm)	Weight of the treated paper (cm)	Ammonia odor after 5 min	Ammonia odor after 40 min
20 x 29.5	15	none	none
19 x 20	10	none	none
20 x 10.5	5	slight	none
10 x 14.5	4	moderate	none
9 x 10	3	strong	none

20

Example 2

(i) Preparation of powdery composition of the iron (II) Compound

25

Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and L-ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$) were mixed and dissolved in 1 : 0.01 molar ratio to prepare an aqueous solution (the total concentration of the ferrous sulfate and ascorbic acid was about 28 % by weight), in which 4 % alum was dissolved. 500 g of the aqueous solution was spray-dried by using a spray drier (DL-21 manufactured by Yamato Kagaku K.K.) under the following conditions to combine the ferrous sulfate, and L-ascorbic acid to obtain a powdery composition containing alum (pH about 3.0).

Operation condition

Liquid feed rate	40 ml/min
Spraying air flow rate	15 l/min
Drying air flow rate	6 m^3/min
Inlet temperature	120 °C
Exit temperature	75 °C

(Film formation by inflation method)

Then, 90 parts by weight of the master pellet of polypropylene and 10 parts by weight of the powdery composition of the iron (II) compound as described above were kneaded in a kneader at 200 - 250 °C to form a premix. Further, 90 parts by weight of polypropylene were added to 10 parts by weight of the premix and kneaded at 220 °C to form a film of 0.05 mm thickness by means of aeration (containing 1 % by weight of iron (II) compound composition).

55

(ii) Freshness-preserving test

10 lemons, 10 melons and 10 peaches bought from a market were divided into two groups. Each piece of fruit in the first group was wrapped separately in a polypropylene film (cut from 24 x 30 cm into an appropriate size) containing the iron (II) compound composition, and hermetically sealed by welding with

the electrically heated seal while each piece of fruit in the second group was wrapped and hermetically sealed in the same manner with a commercially available plastic bag. They were tightly closed in an ordinary manner with no evacuation in either of the groups. They were preserved at an ambient temperature (28 °C) and observed for the freshness (chromaticity and luster on the epidermis, generation of mold, 5 hardness of the pulp, the state of the bisected pulp, state of the calyx or the like). The results are shown in Table 3. As apparent from the results of the table, those wrapped with the film according to this invention can be preserved longer by about 2 weeks in the case of lemon and melon and for about one week longer even those perishable fruits such as peaches compared with the case when conventional films are used.

10

(iii) Deodorizing Test

The deodorizing test was carried out by using a test device assembled as shown in Figure 2. In the figure, are shown a tetra-pack 1, a flowmeter 2, a column 3, and a pump 5. Five grams of polypropylene 15 films according to this invention prepared in the same manner as above and finely cut each into about 5 mm square were placed at 4 of the column and NH₃ gas was charged at 1700 ppm and 240 ppm concentration respectively in the tetra-pack 1 and the entire system was connected. After circulating the gas for one hour through the system, the concentration was measured for the first time. Then, the NH₃ gas was 20 replaced with fresh one at an identical concentration and the test was carried out in the same manner (the polypropylene specimens were used not replaced). In this way, the identical experiments were repeated for six times and the results are shown in Table 4 and Table 5.

25

30

35

40

45

50

55

Table - 3

	2nd day	4th day	6th day	7th day	10th day	13th day	15th day	17th day	19th day	20th day	21st day
This invention	no change	no change	no change	no change	calyx recovered green with luster, and pulp was hard	calyx remained green with luster, and pulp was hard	calyx remained green with luster, and pulp was hard	calyx remained green with luster, and pulp was hard	calyx remained green with luster, and pulp was hard	pulp was fresh and taste sour	
Lesson											
Comparative invention	no change	no change	epidermis lost luster	epidermis discolored, pulp softened	epidermis blackened, luster lost and pulp softened further	started to partially perish	rot developed and deformation released completely	deformation occurred, slime released	no particular change, with luster	white mold occurred, partially, but pulp remained hard	dissected pulp was sound
This invention	no change	no change	no change	no change	white mold occurred partially	white mold occurred entirely, pulp softened	entirely covered with white mold, pulp softened	dissected pulp was disintegrated, entirely softened with putrid odor			
Melon											
Comparative Example	no change	white mold occurred partially	white mold extended, pulp softened	white mold extended, pulp softened	white mold occurred entirely, pulp softened	white mold occurred entirely, pulp softened	white mold occurred entirely, pulp softened	epidermis lost tension slightly	epidermis partially turned dark brown	dark brown area of the epidermis extended, pulp softened	dark brown area of the epidermis further extended, pulp softened entirely
This invention	no change	no change	no change	no change	no change	no change	no change	no change	completely perished		
Peach											
Comparative Example	no change	no change	epidermis partially turned dark brown	dark brown area extended	turned dark brown entirely, started to perish						

Table 4

Ventilation (cycle)	1	2	3	4	5	6
Residual concentration (ppm)	740	1200	1300	1400	1450	1500

(note) Test condition

Offensive odor gas	NH ₃
Gas concentration	1700 ppm
Gas flow rate	1 l/min
Ventilation time	60 min
Column diameter	24 mm ♂
Bed height	55 mm
Air temperature	25°C
Sample	pp sheet (kneaded with 1.0 % iron (II) compound composition)
Sample weight	5 g

Table 5

Ventilation (cycle)	1	2	3	4	5	6
Residual concentration (ppm)	100	140	160	170	180	190

(note) Test condition

Offensive odor gas	NH ₃
Gas concentration	240 ppm
Gas flow rate	1 l/min
Ventilation time	60 min

Column diameter	24 mm Ø
Bed height	55 mm
5 Air temperature	27 °C
Sample	pp sheet (kneaded with 1.0 % iron (II) compound composition)
10 Sample weight	5 g

15

Example 3 (Freshness-preserving agent)

After dissolving 27.5 g of ferrous sulfate heptahydrate (molecular weight 278.03) with water to 100 ml, 0.5 g of L-ascorbic acid was added and dissolved to prepare an undiluted aqueous solution of iron L-ascorbate.

20 Then, after dissolving 3 % by weight of alum into the undiluted solution, it was diluted twice with water to prepare an active aqueous solution.

25 On the other hand, an apparatus comprising a vinyl plastic housing 91 cm width x 54 cm depth x 154 cm height) having a well ventilated medium shelf for placing foods and having a forcible humidifier (ventilating amount, 1.2 liter/min) at the lower part of the inside (several mm of gaps are intentionally disposed to the joining portions for each of the sides) was assembled and the humidifier was operated after charging 20 liter of the freshness-preserving aqueous solution into the humidifier.

30 Then, bananas (6 pieces in one bunch), raw shiitake (6 pieces), lemon (4 pieces), bought from the market were divided into two groups, of which one of the groups was placed on the shelf within the vinyl plastic housing and the other was left in the room outside the vinyl plastic housing. The aging change in the 35 freshness of each of the foods was observed for 7 days with naked eyes. When the stationary state was attained after operating the humidifier, the temperature was 18 °C and the humidity was 90 %. The room temperature was 19 °C and humidity was 70 % outside the vinyl plastic housing. The test results are shown in the Table 6 below.

35 From the results of the Table below, while the pulp softened and black bruises were increased in bananas when left at the room temperature for 7 days, it was observed for those bananas treated with the method according to this invention that the pulp did not soften but, rather, bruises in the epidermis were restored and disappeared. Accordingly, it can be seen that excellent freshness-preserving and quality-improving effects can be obtained by the method according to this invention. Furthermore, it is apparent 40 that the freshness can also be preserved for a long period of time also in the case of raw shiitake and lemon by the method according to this invention. In the case of lemon, particularly, it is noted that the luster of the epidermis increased with the lapse of days.

45

50

55

5
10
15
20
25
30
35
40
45
50
55

Table 6

Days of preservation	Banana	Pawpaw	Lesson
This invention	no change	no change	no change
Comparative example	no change	no change	no change
1st day	epidermis yellow rather intense	no change	no change
This invention	epidermis yellow rather intense	no change	no change
Comparative example	no change	no change	no change
2nd day	epidermis yellow further increased	no change	no change
This invention	epidermis yellow further increased, black bruises decreased	no change	epidermis recovered luster
Comparative example	black bruises on the epidermis increased a little	white areas under the cap slightly turned brown	no change
3rd day	black bruises gradually decreased and epidermis recovered tension	no change	epidermis yellow became deep. luster increased further
This invention	black bruises gradually extended	brown spots increased in the white area below the cap	luster lost and discolored
Comparative example	black bruises almost disappeared, hardness increased	no change	luster increased further, the pulp hardened
4th day	black bruises gradually extended	brown spots in the white pulp increased, discoloration recognized	discolored, pulp softened
This invention	black bruises almost disappeared, hardness increased	brown spots in the white pulp increased, discoloration recognized	brilliant color, hard pulp
Comparative example	black bruises extended, pulp softened	good luster at the dark brown area of epidermis calyx color showed no change	
5th day	black bruises entirely disappeared, hardness recovered	calyx brown color was deepened	
This invention	black bruises extended, softness increased	entire appearance was fine, pulp was strong	good luster at the dark brown area of epidermis, no brown spots recognized in the white pulp
Comparative example	black bruises increased entirely, discolored and softened further	brown spots in the white area extended, white spots appeared in the dark brown surface epidermis	pulp lost luster, softened and tasted less sour
6th day			
This invention			
Comparative example			
7th day			

Example 4

5

(I) Growth promoting test for flowers and ornamental plants

An active aqueous solution was prepared in the same manner as in Example 3.

10 An apparatus comprising a vinyl plastic housing (91 cm width x 54 cm depth x 154 cm height) having a well-ventilating medium shelf for placing plant pots and equipped with a forcible humidifier (ventilation amount 1.2 l/min) at the lower part of the inside was assembled near the window within a room provided with slight (several mm) of gaps at the joining portions for each of the sides), and the humidifier was operated after charging 20 liter of the active aqueous solution into the humidifier.

15 Then, respective one pot of syunran (*cymbidium goeringii* rech f.), hanakilin (crown of thorns) and kinkouka (*narthecium asiaticum*) which had been bought each by two pots as the test plants were placed on the shelf within the vinyl plastic housing while other pots were left in the room outside the vinyl plastic housing and the change in the growth of the plants was observed. When the stationary state was attained after operating the humidifier, the temperature was 18 °C and the humidity was 90%. The room temperature was 19 °C and humidity was 70% outside the vinyl plastic housing. The test results are shown in Table 7.

25

30

35

40

45

50

55

5
10
15
20
25
30
35
40
45
50
55

Table 7

Days of treatment	Item of the observation	<i>Solanum</i> (Cymbidium socorinkii Rech. f.)		<i>Kinabalu</i> (Narthecium agathicium)	
		extension of stalks and buds	color of leaves and buds	extension of stalks and buds	color and luster of leaves and stalks
1st day	This invention	no change	no change	no change	no change
	Comparative example	no change	no change	no change	no change
2nd day	This invention	stalk developed 5 mm	no change	brown stalk portion turned bluish	green deepened
	Comparative example	no change	no change	no change	no change
3rd day	This invention	stalks developed about 1 cm	green color deepened	buds emerged from the stalks, green leaves emerged	luster on the leave surface increased
	Comparative example	no change	no change	no change	no change
4th day	This invention	stalks developed about 1 cm, buds emerged	—	green leaves increased	stalk tip turned green
	Comparative example	no change	no change	—	luster on the leave surface further increased
5th day	This invention	stalk developed about 1 cm	green color further deepened	pale pink bud extended	leaf surface glintened, the surface got luster
	Comparative example	no change	no change	no change	no change
6th day	This invention	stalk developed about 1 cm	green color deepened, bloomed	pale pink bud extended entirely from the tip	luster on both faces of leaves increased further
	Comparative example	no change	no change	no change	no change

(note) 1. Test was carried out at the end of February.
 2. In the table "no change" means there was no remarkable changes.

(ii) Growing test for paddy field rice plant

5

(Aqueous agent)

A solution prepared by dissolving 3 % by weight of alum in the undiluted aqueous solution of iron L-ascorbate as prepared in Example 3 (hereinafter referred to as the aqueous agent according to this invention) was used.

The aqueous agent according to this invention, commercially available photosynthetic bacteria or ordinary water was applied to the soils of paddy field rice plants and the difference in the growing states was observed.

15 Step 1 : Growth was observed for the group of seedlings grown to about 5 cm height in the nursery bed in the case of using water incorporated with the aqueous agent according to this invention and ordinary water (before transplantation)

Step 2 : Change in the growth was observed in the paddy field (foamed styrol box) supplied with water containing the aqueous agent according to this invention, incorporated with photosynthetic bacteria and ordinary water after transplantation.

20 Step 3 : The state of hull and rice were observed at the stage of ripening.

(Test Method)

25

1. Kind of soils used

Commercially available black soils and Arakida soil were mixed (2 : 1).

30

2. Observation for the growth in the nursery bed

Observation was made for the test lot divided into three lots.

35 (1) First lot : Grown only with tap water (referred to as tap water lot)
 (2) Second lot : Grown with 100 times diluted aqueous solution according to this invention (100 times lot)
 (3) Third lot : Grown with 400 times diluted aqueous solution according to this invention (400 times lot)
 40 (4) Fourth lot : Grown with 1000 times diluted aqueous solution according to this invention (1000 times lot)

3. Observation for the growth after transplantation

45 After confirming the rooting of the seedlings after the lapse of five days from the transplantation, the composition of water in the paddy field was changed as below.

(1) Lot A : 100 cc of a solution prepared by adding 5 % photosynthetic bacteria to the 40 times diluted aqueous solution according to this invention was applied to the paddy field of 400 times lot
 50 (2) Lot B : 100 cc of the 40 times diluted solution of the aqueous agent according to this invention was applied to the paddy field of the 100 times lot.
 (3) Lot C : 100 cc of the 40 times diluted solution of the aqueous agent according to this invention was applied to the paddy field of the 400 times lot.
 55 (4) Lot D : Several drops of photosynthetic bacteria were added to the paddy field of the 1000 times lot.
 (5) Lot E : Only tap water was added to the paddy field of the tap water lot.
 (note) Adjustment of the water for the paddy field was carried out only once and subsequent supply of water

was conducted with tap water in all of the cases.

(Test Result)

5

1. Growing state in the nursery bed (after elapse of three weeks)

10 It took three weeks to reach the aimed seedling height of 10 cm, in which the seedlings in the lot C (400 times lot) were higher than the seedling in other lots and they showed remarkable deep green color. There was no difference in other lots.

2. 16th day after the transplantation

15

(1) The growth of the seedling in the lots B and C was twice that of seedlings in other lots, and the green color was deepened. The growth was satisfactory.

(2) The growth of the seedlings in the lot A was next to the above and the height of the seedlings was about 2/3. They turned slightly yellow.

20

(3) In the lots D and E, the height of the seedlings was about 1/2 that in the lots A, B and they exhibit some yellowing in the leaves. The growth was poor.

3. 27th day after the transplantation

25

The height of seedlings extended well, in which the growth in the lots B, C was outstanding. Since a slight sign of yellowing was observed, it was judged that the fertilizer was almost exhausted and a handful of a mixture of organic synthetic fertilizer and oil cake was applied to all of the lots.

30

4. 32th day after the transplantation

Green color was recovered from yellowing all over the lots. Particularly, the green color was deepened in the lots B, C where remarkable growth was exhibited. The diameter of the stalks in the above lots was twice as large as in other lots.

35

5. 57th day after the transplantation

40 Earing was seen in the rice plants in the lots A, B, C, E. No emergence of the ears was found in the lot D only. Particularly, ears in the lots B, C seemed sound and a number of hulls were counted in the lots B, C.

45

6. 60th day after the transplantation

Ears were completely emerged in all of the lots.

50

7. 70th day after the transplantation

Ears were beginning to sag in the lots B, C. The hulls were solid. Ripening in the lot A was next to the lots B, C. Hulls were empty in lots D, E. The test results are shown in the table below.

55

Table 8

Test lot	Number of hauls	Size of grain	Length of stalk	Length of root
Lot A	40 - 45	small	50 - 55 cm	13 cm
Lot B,C	55 - 60	large	65 - 70 cm	17 cm
Lot D,E	20 - 23	none	43 - 45 cm	10 cm

Summarizing the results of the test as above, it was judged that the rice plants in the lots B, C were grown as in the rich harvest type, the rice plants in the lot A showed somewhat poor growth and the rice plants in the lots D, E were grown quite in the bad harvest type. It was confirmed that a significant desirable effect was given for the growth of the paddy field rice plants by adding the aqueous agent according to this invention at the initial stage of the growing. In addition, a further development can be expected by applying a fertilizer to the soils upon transplantation.

20

Example 5

An aqueous ink was prepared in the following composition, which was coated on an embossed wall paper made of vinyl chloride resin (the coating thickness of the vinyl chloride sol between 160 - 200 μ) by the spanishing method using a doctor knife.

Aqueous ink		(parts by weight)
30	VPA G medium	90
	VPA G color	10
35	Aqueous solution of iron (II) composition	20
Total		120

40

The coating conditions are as below.

45 Coating amount : about 30 g/m²
 Treating rate : 15 m:min
 Drying temperature : 120 °C for one min.

The aqueous solution of iron (II) composition was prepared by dissolving 27.5 g of ferrous sulfate heptahydrate (molecular weight 278.03) in water to make up 100 ml and adding and dissolving 0.5 g of L-ascorbic acid to prepare an undiluted solution and, thereafter, adding 10 g of burnt alum to 100 ml of the undiluted solution, stirring for 30 min and centrifugally separating them, followed by filtration.

The results of the test for the air cleaning effect on the thus treated wall paper is shown as the tests (i) - (iii).

55

Test (i)

After placing filter paper (filter paper 14 in 9 cm diameter) impregnated with chemicals such as

5 formalin, artificial sweat and ammonia at the concentration as described below each by about 0.45 g in a polyethylene-made bag of 25 x 30 cm and further placing wall paper of 10 cm² specimens treated as described above on to the bottom of the bag, the intensity of the odor in the bag was tested. The results are shown in Table 9 as the Test No. 1. The test was further carried out for the case where the wall paper 10 specimens were further heated at 180 °C for 20 sec (corresponding to emboss fabrication condition) or at 230 °C for one min (corresponding to forming fabrication condition) and the results are also shown in Table 9 as the Test No. 2 and No. 3. Concentration of Chemicals

10 (1) Formalin : aqueous 5 % solution
 (2) Artificial sweat solution : prepared according to JIS K 6772
 (3) Ammonia : aqueous 1.25 % solution
 (4) Cresol : aqueous 1 % solution
 (5) hydrogen sulfide : an aqueous solution prepared by passing gaseous hydrogen sulfide through water for 5 min.

15

Table 9

Test No.	1	2	3
Heating	-	180 °C x 20 sec	230 °C x 1 min
Formalin	1 min	3.8	3.7
	5 min	3.1	3.6
Artificial sweat solution	1 min	2.4	2
	5 min	1.1	1.3
Ammonia	1 min	2.8	2.3
	5 min	1.6	1.4
Hydrogen sulfide	1 min	2.5	2.0
	5 min	1.6	1.7
Cresol	1 min	2	2.2
	5 min	1.3	2.0

45

(note) Evaluation standards

46

- 1 no odor
- 2 slight odor
- 3 considerable odor
- 4 original odor did not change

50

55 Numerical values of the data represent the average value for 10 test panelers.

Test (ii)

Then, the test was carried out for the deodorizing effect of the wall papers when placed in usual atmosphere for certain period of time. The test was carried out on the wall papers heated at 230°C for one min. The test results are shown in Table 10.

5

Table 10

Chemicals	Date of measurement	59.5.10 n = 5	59.5.18 n = 3	59.5.29 n = 4	59.6.7 n = 4	59.7.11 n = 4
Ammonia	1 min	2.8	2	3.6	2.5	2.5
	5 min	1.6	1.5	2.8	1.7	1.8
Cresol	1 min	2	2.5	2.9	3.4	3.0
	5 min	1.3	1.8	2.0	2.9	2.0
Artificial sweat solution	1 min	2.4	2.3	2.3	2.6	2.5
	5 min	1.1	1.5	2.1	1.9	1.9
Formalin	1 min	3.8	2.7	3.9		
	5 min	3.1	2.5	3.9		

(note) The evaluation standards are the same as those in

30

Table 9.

35 It is estimated from the results of the foregoing functional test that the wall papers according to this invention exhibit the deodorizing effect against offensive odor substances (excepting for formalin) generated in daily life, that the effect is not reduced by heating (about 230°C x one min) at all and that the effect undergoes no remarkable alteration due to aging change but is retained for a considerable period of time.

40 Since the atmospheric concentration used in the foregoing test is such a high level as is not usually experienced in the daily life, and since the effect is maintained under these conditions, it means that the wall papers can endure the long period of use.

Test (iii)

45 Then, a deodorizing test was carried out by using a test apparatus assembled as shown in Figure 2 in the same manner as in the deodorizing test (iii) in Example 2. Five grams of wall paper specimens finely cut into about 5 mm squares were placed in C and NH₃ gas at 5000 ppm concentration was charged in A in the drawing and the entire system was connected. After circulating the gas for one hour, the concentration was measured. Then, a fresh gas (NH₃ concentration at 5000 ppm) was charged in A (the wall paper specimens were placed as they were although the NH₃ gas was changed) and the similar experiments were repeated four times. The result of the four times of the experiment are shown in Table 11.

Table 11

Ventilation (cycle)	1	2	3	4
Residual concentration (ppm)	1050	4000	4500	4800

(note) Test Condition

Offensive odor gas	NH ₃
Gas concentration	5,000 ppm
Gas flow rate	1 l/min
Ventilation time	80 min
Air temperature	27 °C
Column diameter	24 mmφ
Bed height	68 mm
Sample	wall paper
Sample weight	5 g

Example 6

(Preparation of Aqueous composition)

The aqueous solution of the following composition was prepared.

45

50

55

Table 13

Composition (parts by weight)	Experiment No.	This invention			Comparative Example 4
		1	2	3	
Ferrous sulfate heptahydrate		25	25	25	25
Burnt alum		3	3	3	3
Citric acid		3	-	3	3
L-ascorbic acid		-	0.5	0.5	-
Sodium chloride		3	3	3	-
Dithionite		0.3	0.3	0.3	0.3
Water		balance	balance	balance	balance
Total		100	100	100	100

25 When water draining garbage bags made of white Japanese paper were immersed in this solution and then dried spontaneously, they were colored pale yellow with no unevenness in the solution of experiment No. 1 - 3 (solid deposition amount 15 % by weight). They were stable after the elapse of one month. While on the other hand, the bag immersed with the aqueous solution of experiment No. 4 was scarcely colored only with extremely pale color after the drying, but it exhibited color of brown iron rust after the elapse of one month it lost its commercial value.

(Deodorizing Test)

35 When the Toyo Filter Paper Teisei No. 2 was immersed in the aqueous solutions of the experiment No. 1 - 3 and 4 and then spontaneously dried, to prepare treated papers 1 - 4 with solid deposition amount of 20 based on 100 of the initial filter paper weight respectively.

40 Then, a deodorizing test was carried out by using a test device assembled as shown in Figure 2 in the same manner as the deodorizing test (iii) in Example 2. Five grams of the treated paper 1 or 4 prepared as above and finely divided into about 5 mm square were placed in C. NH_3 gas at 1700 ppm or 18000 ppm concentration was charged into A and the entire system was connected. After recycling the gas for one hour, concentration was measured for the first time. Then, the same test was carried out, replacing the gas with the fresh NH_3 gas at the same concentration (the treated paper specimens were left unchanged). In this way, the identical experiment was repeated 8 times. The results are shown in Table 14 and Table 15.

50

55

Table 14

Ventilation (cycle)	1	2	3	4	5	6	7	8
Residual concentra- tion (ppm)	0.4	0.5	0.8	5.5	15	40	160	3800

10

(note) Measuring Condition

Offensive odor gas	NH ₃
Gas concentration	18000 ppm
Gas flow rate	1 l/min
Ventilation time	60 min
Air temperature	26°C
Column diameter	24 mmØ
Bed height	52 mm
Sample	treated paper 1
Sample weight	5 g

Table 15

Ventilation (cycle)	1	2	3	4	5	6	7	8
Residual concentra- tion (ppm)	1.0	1.0	3.5	2.0	5.0	30	330	7500

45

50

55

(note) Measuring Condition

5	Offensive odor gas	NH ₃
10	Gas concentration	17000 ppm
	Gas flow rate	1 l/min
15	Ventilation time	60 min
	Air temperature	27 °C
20	Column diameter	24 mmØ
	Bed height	75 mm
	Sample	treated paper 4
25	Sample weight	5 g

(Flame-proofing test)

25 A flame of 4 cm flame length was prepared by a gas burner of 1 cm inner diameter while not mixing air with gas, and then treated papers 1 - 3 were put into the flame for two sec from the top end of the flame for 2 cm length, but they neither produced flame nor burnt, only remaining the carbonized products.

30 Then, by impregnating formed urethane sheet with the aqueous compositions, experiment No. 1 - 3 and 4 as described above to prepare treated urethane material with 20 % by weight of the solid content. They were subjected to flame proofing test in the same manner as described above. Although experiment No. 4 burnt with flame, experiment No. 1 - 3 neither produced flame nor burnt only becoming carbonized products.

35

Claims

1. A chemically active composition containing divalent iron ions, wherein a water soluble iron (II) compound, alum and ascorbic acid and/or citric acid are contained, and the ratio between the divalent iron ions in the iron (II) compound and ascorbic acid or citric acid is between 1:0.02 and 0.30 (in the case of ascorbic acid) or 1:0.01 and 0.80 (in the case of citric acid) by weight ratio; and wherein the alum is contained within a range up to 100 % by weight based on the total amount of the iron (II) compound, ascorbic acid and/or citric acid.
2. The composition as defined in claim 1, wherein alum is contained from 2 to 100 % by weight.
3. The composition as defined in claim 1, wherein the amount of alum is from 2 to 20 % by weight.
4. The composition as defined in claim 1, which is an aqueous solution.
5. The composition as defined in claim 1, which is a drying product of the aqueous solution.
6. The composition as defined in claim 1, which contains sodium chloride in an amount of from 0.5 to 15 % by weight based on the total amount of the iron (II) compound, ascorbic acid and/or citric acid.
7. A deodorant, freshness-preserving agent for foods, growth promoting agent for plants and flame-retardant for burnable materials comprising the composition as defined in claim 1.

8. A multi-functional material prepared by incorporating the composition as defined in claim 1 by way of impregnation, coating, dipping, spraying or kneading
9. The composition as claimed in claim 1, wherein the ratio between the divalent iron ions in the iron (II) compound and ascorbic acid is in the range of 1:0,02 to 1:0,13.
10. A method of food preservation by applying to said foods a food preservative effective amount of the composition of claim 4 or 5.
11. A method of promoting the growth of plants by adding to said plants a growth promoting effective amount of the composition of claim 1.
12. A method of flame retardation by adding to a burnable material a flame retarding effective amount of the composition of claim 4 or 5.
13. A method of deodorizing by adding to offensive odors a deodorizing effective amount of the composition of claim 4 or 5.

20 **Revendications**

1. Composition chimiquement active contenant des ions fer divalents, dans laquelle sont contenus un composé de fer (II) soluble dans l'eau, de l'alun et de l'acide ascorbique et/ou de l'acide citrique, et le rapport entre les ions fer divalents dans le composé de fer (II) et l'acide ascorbique ou l'acide citrique est compris entre 1:0,02 et 0,30 (dans le cas de l'acide ascorbique) ou 1:0,01 et 0,80 (dans le cas de l'acide citrique) en rapport pondéral ; et dans laquelle l'alun est contenu dans un intervalle allant jusqu'à 100 % en poids basé sur la quantité totale de composé de fer (II), d'acide ascorbique et/ou d'acide citrique.
2. Composition selon la revendication 1, dans laquelle l'alun est contenu entre 2 et 100 % en poids.
3. Composition selon la revendication 1, dans laquelle la quantité d'alun est de 2 à 20 % en poids.
4. Composition selon la revendication 1, qui est une solution aqueuse.
5. Composition selon la revendication 1, qui est un produit séchant de la solution aqueuse.
6. Composition selon la revendication 1, qui contient du chlorure de sodium en une quantité de 0,5 à 15 % en poids basé sur la quantité totale de composé de fer (II), d'acide ascorbique et/ou d'acide citrique.
7. Déodorant, agent de conservation de la fraîcheur pour aliments, agent promoteur de croissance pour les plantes et retardateurs de flamme pour des matières inflammables comprenant la composition selon la revendication 1.
8. Matériau multifonctionnel préparé en incorporant la composition selon la revendication 1 par voie d'imprégnation, de revêtement, par immersion, par pulvérisation ou pétrissage.
9. Composition selon la revendication 1, dans laquelle le rapport entre les ions fer divalents dans le composé de fer (II) et l'acide ascorbique se situe dans l'intervalle de 1:0,02 à 1:0,13.
10. Procédé de conservation des aliments en appliquant auxdits aliments une quantité efficace pour la conservation d'aliments de la composition selon la revendication 4 ou 5.
11. Procédé pour accélérer la croissance des plantes en additionnant auxdites plantes une quantité efficace promoteur de croissance de la proposition selon la revendication 1.
12. Procédé de ralentissement de flamme en additionnant à une matière inflammable une quantité efficace pour retarder la flamme de la composition selon la revendication 4 ou 5.

13. Procédé pour désodoriser en additionnant aux odeurs déplaisantes une quantité efficace pour désodoriser de la composition selon la revendication 4 ou 5.

5 Ansprüche

1. Eine chemisch aktive Zusammensetzung mit einem Gehalt an zweiwertigen Eisenionen, wobei eine wasserlösliche Eisen-II-Verbindung, Aluminiumoxid und Askorbinsäure und/oder Zitronensäure enthalten sind und das Verhältnis zwischen den zweiwertigen Eisenionen in der Eisen-II-Verbindung und Askorbinsäure oder Zitronensäure im Bereich von 1:0,02 und 0,30 (für Askorbinsäure) oder 1:0,01 und 0,80 (für Zitronensäure) auf Gewichtsbasis liegt und wobei das Aluminiumoxid in einem Bereich von bis 100 Gew.-% auf Basis der Gesamtmenge der Eisen-II-Verbindung, der Askorbinsäure und/oder der Zitronensäure enthalten ist.
2. Zusammensetzung nach Anspruch 1, wobei das Aluminiumoxid im Bereich von 2 bis 100 Gew.-% enthalten ist.
3. Zusammensetzung nach Anspruch 1, wobei die Menge an Aluminiumoxid im Bereich von 2 bis 20 Gew.-% liegt.
4. Zusammensetzung nach Anspruch 1, wobei die Zusammensetzung eine wässrige Lösung ist.
5. Zusammensetzung nach Anspruch 1, wobei die Zusammensetzung ein Trocknungsprodukt der wässrigen Lösung ist.
6. Zusammensetzung nach Anspruch 1, wobei die Zusammensetzung Natriumchlorid in einer Menge von 0,5 bis 15 Gew.-% auf Basis der Gesamtmenge an Eisen-II-Verbindung, Askorbinsäure und/oder Zitronensäure enthält.
7. Doedoranz, Frischhaltemittel für Nahrungsmittel, Wachstumsförderungsmittel für Pflanzen und Flammhemmmittel für brennbare Materialien, umfassend die Zusammensetzung gemäß Anspruch 1.
8. Multifunktionales Material, dadurch hergestellt, daß die Zusammensetzung gemäß Anspruch 1 durch Imprägnieren, Überziehen, Eintauchen, Sprühen oder Kneten einverlebt worden ist.
9. Zusammensetzung gemäß Anspruch 1, wobei das Verhältnis zwischen den zweiwertigen Eisenionen in der Eisen-II-Verbindung und der Askorbinsäure im Bereich von 1:0,2 bis 1:0,13 liegt.
10. Verfahren zur Nahrungsmittelkonservierung, bei dem man auf die Nahrungsmittel eine die Nahrungsmittel konservierende wirksame Menge an der Zusammensetzung gemäß Anspruch 4 oder 5 aufbringt.
11. Verfahren zur Förderung des Wachstums von Pflanzen, bei dem man auf die Pflanzen eine das Wachstum fördernde Menge der Zusammensetzung gemäß Anspruch 1 aufbringt.
12. Verfahren zur Flammhemmung, bei dem man auf ein brennbares Material eine zur Flammhemmung wirksame Menge der Zusammensetzung gemäß Anspruch 4 oder 5 zufügt.
13. Verfahren zur Deodorierung, bei dem man einem aktiven Geruch eine zur Deodorierung wirksame Menge der Zusammensetzung gemäß Anspruch 4 oder 5 zufügt.

50

55

FIG. I

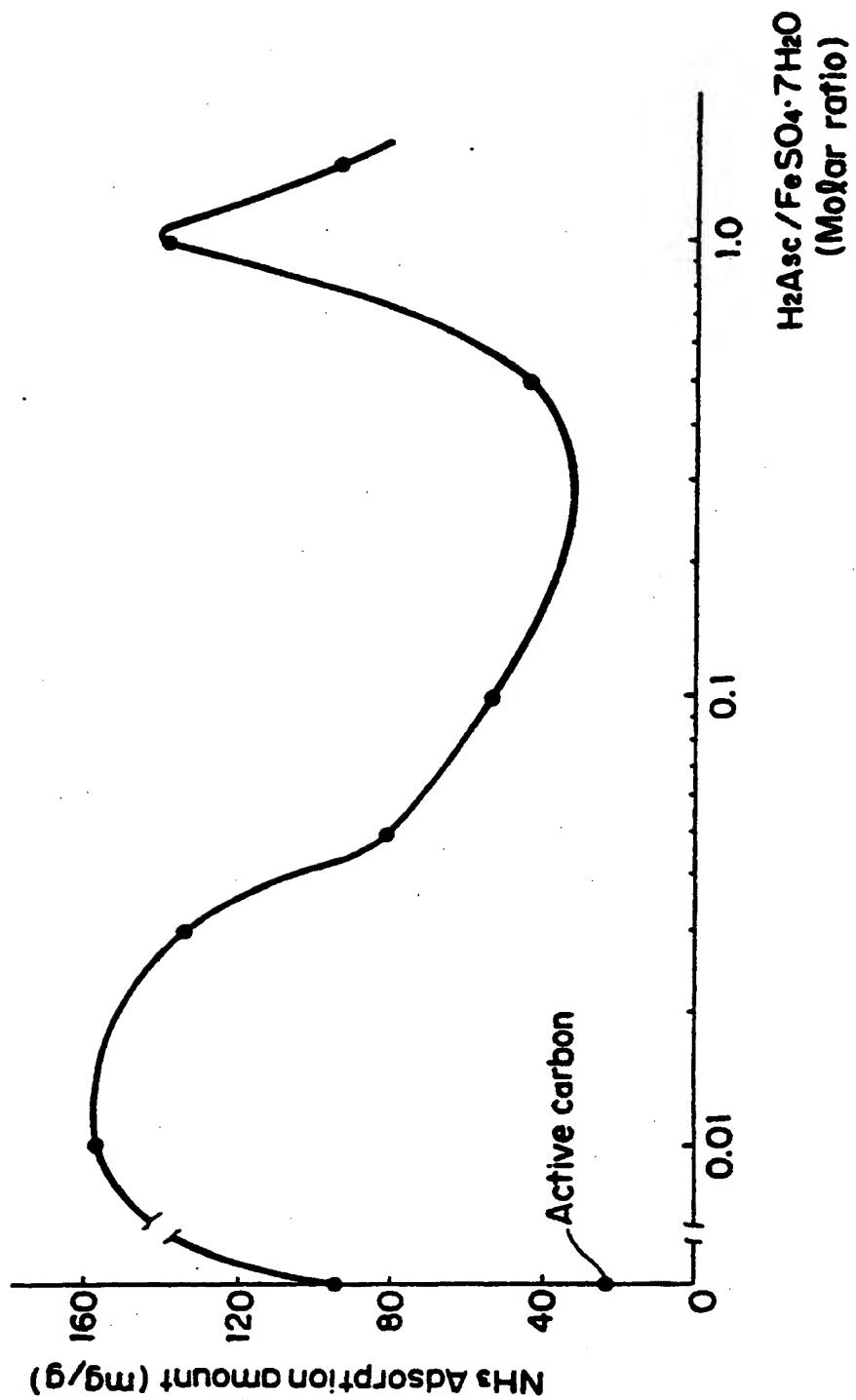


FIG.2

